

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

com. to de 23 06 667

# PATENT SPECIFICATION

(11) 1449316

1449316

- (21) Application No. 5795/74 (22) Filed 8 Feb. 1974  
(31) Convention Application No. 2306667 (32) Filed 10 Feb. 1973 in  
(33) Germany (DT)  
(44) Complete Specification published 15 Sept. 1976  
(51) INT CL<sup>2</sup> C08F 10/08 4/66  
(52) Index at acceptance

C3P 102 13G4B 13G7B1 13G7Y 13G8A 13G8Y 13N2 7D1A  
7D1C 7D1D 7K7 D11 P5



## (54) PROCESS FOR THE MANUFACTURE OF LARGELY AMORPHOUS BUTENE-1 POLYMERS

(71) We, CHEMISCHE WERKE HÜLS AKTIENGESELLSCHAFT, a German Company, of 4370 Marl, Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The application relates to a process for the manufacture of largely amorphous butene-1 polymers by the low-pressure method.

For various fields of use, for example for coating and sealing compositions and for casting compositions and adhesives, substantially amorphous polyolefins, especially substantially amorphous polybutene-1, are required.

It is known to prepare amorphous polymers by polymerisation of  $\alpha$ -olefinic hydrocarbons with catalysts which have been obtained by reaction of compounds of metals of sub-group IV to VI of the periodic system, including thorium and uranium, with organo-metallic compounds of metals of group II or III of the periodic system, especially of aluminium, magnesium or zinc.

According to German published patent application DAS 1,795,483, the catalysts employed should be liquid or dissolved or finely disperse and should preferably be obtained from liquid, or hydrocarbon-soluble, compounds of the metals of sub-group IV to VI of the periodic system, in their maximum valency. If the catalysts are not liquid or dissolved, suitable measures must be taken to produce a fine degree of dispersion. In contrast, polymerisation with catalysts which are more coarsely disperse or contain more crystalline particles is supposed to lead to predominantly or exclusively isotactic and crystalline polymers. Hence, the more finely disperse parts should be isolated by filtration, decanting sedimentation, centrifuging or similar methods. Furthermore, for example, the reduction of titanium tetrachloride should be carried out under such conditions that no crystalline constituents, or only the minimum

possible amounts of such constituents, are formed.

According to the statements of that German published patent application, an important possible way of manufacturing amorphous, atactic polymers is to use, as starting substances, heavy metals which are present in a higher state of valency, especially in their maximum valency. It is furthermore demanded that to manufacture polyolefins which are predominantly or exclusively amorphous and non-isotactic in nature, the process should start from liquid or dissolved catalysts and in preparing these dissolved catalyst care should be taken to ensure that the catalysts really do dissolve. It is furthermore regarded as desirable that the catalysts should be prepared using lyophilic groups such as hydroxyl or alkoxy groups.

Organo-metallic compounds with alkyl groups containing more than 4, preferably 6 to 16, carbon atoms, should be employed for the activation. Activation with organo-metallic compounds which contain halogen atoms in addition to alkyl groups is supposed to direct the polymerisation ultimately towards the production of polyolefines which are predominantly or exclusively amorphous in nature.

Surprisingly, however, this process is unsuitable for the manufacture of largely amorphous polybutene-1 and its copolymers. Thus, if organo-metallic compounds containing halogen, for example aluminium-diethyl chloride, are used for the activation, polybutene-1 with a substantially higher instead of lower crystallinity is obtained. A polymerisation with heavy metal compounds containing hydroxyl or alkoxy groups, such as, for example, chlorotitanic acid esters, titanium tetraesters and titanium hydroxide is virtually not possible in the case of butene-1 as the monomer, because of the low activity of the contact catalyst even at higher contact catalyst concentrations. Polymerisation of butene-1 with aluminium-alkyl compounds containing alkoxy groups is also practically ruled out because of the contact catalyst

activity being too low. Equally, the liquid or hydrocarbon-soluble heavy metal compounds recommended as being preferred have only an inadequate activity in the polymerisation of butene-1 to amorphous polybutene-1. The same is true for contact catalysts with organo-metallic compounds, containing alkyl groups with more than 4 carbon atoms, in the case of the polymerisation of butene-1.

Accordingly, there exists the problem of providing a usable process for the manufacture of largely amorphous homopolymers, copolymers and terpolymers of butene-1.

According to the invention there is provided a process for the manufacture of a largely amorphous butene-1 polymer by the low-pressure method, wherein butene-1 is homopolymerised or is copolymerised with from 0.1 to 30 per cent by weight based on butene-1 of one or more other  $\alpha$ -monoolefins, in bulk or in solution in a  $C_4$ -fraction containing butene-2 and/or butane in addition to butene-1, at a temperature of 40 to 120°C, using a mixed catalyst consisting of

$TiCl_3 \cdot n AlCl_3$

( $n=0.2$  to  $0.6$ ) and an aluminium trialkyl with  $C_2$ - to  $C_4$ -alkyl groups, at an atomic ratio of Al in the aluminium trialkyl:Ti in the

$TiCl_3 \cdot n AlCl_3$

of from 1.2:1 to 5:1, preferably 1.5:1 to 3:1, and a concentration of 0.01 to 1 mmol of  $TiCl_3$  per litre of total liquid phase.

The butene-1 to be polymerised, which optionally serves at the same time as the sole solvent for the formed polymer and solvent/suspending agent for the catalyst, should be as free as possible of compounds with active hydrogen, especially of water, alcohols and mercaptans, of acetylenic hydrocarbons and of hydrocarbons with multiple unsaturation, such as butadiene, especially butadiene - 1,2 and propadiene, and of oxygen.

Iso-butene in major amounts reduces the rate of polymerisation. The iso-butene component should therefore preferably account for less than 10%, based on butene - 1.

The  $C_4$ -fraction which alternatively serves as the solvent should preferably contain at least 40% of butene-1; the ratio of butene-2 to butane is not critical and preferably the  $C_4$ -fraction produced in the refinery is employed. Pure butene-2 or butane can also be used as the solvent. In mixtures which contain butene-2 in addition to butene-1, the former virtually does not polymerise.

The butene-1 can be polymerised as pure material or mixed with 0.1 to 30 per cent by weight, preferably 1 to 20 per cent by weight, of one or more other  $\alpha$ -monoolefins such as ethene, propene, pentene, hexene-1 or

dodecene-1, preferably propene and ethene. Ethene, hexene-1 and dodecene-1 reduce the crystallinity more than does, for example, propene. Propene is therefore employed in higher proportions.

A suitable

$TiCl_3 \cdot n AlCl_3$

preferably has  $n=0.3$  to  $0.35$  and is in particular the crystalline

$TiCl_3 \cdot 0.33AlCl_3$

obtained by reduction of titanium tetrachloride with aluminium, which according to the statements of German published patent application DAS 1,795,483 is supposed to be completely unsuitable for the manufacture of substantially amorphous polybutene-1. It is not necessary to separate it into fractions which contain more finely disperse and less crystalline particles.

Suitable aluminium trialkyls are aluminium triethyl, aluminium tripropyl, aluminium tributyl and, preferably, aluminium triisobutyl. The mixed catalyst may be prepared by introducing the aluminium trialkyl and the

$TiCl_3 \cdot n AlCl_3$

in appropriate amounts into the polymerisation reactor, for example at the polymerisation temperature. Prior mixing of the components is possible but not essential. The atomic ratio Al in the aluminium trialkyl:Ti in the

$TiCl_3 \cdot n AlCl_3$

in the finished mixed catalyst is particularly preferably from 2.5:1 to 3.0:1.

The activity of this mixed catalyst is excellent. The polymerisation can therefore be carried out even at very low concentrations of the catalyst, for example from 0.01 to 0.3 mmol of  $TiCl_3$ /l. For this reason, the catalyst is employed in the polymerisation in amounts to provide from 0.01 to 1, preferably 0.05 to 0.3, mmol of  $TiCl_3$  per litre of the total liquid phase. Larger amounts of catalyst are necessary if impurities are present than if the materials are pure.

The molecular weight may be regulated during the polymerisation, e.g. in a manner which is in itself known, preferably by addition of hydrogen to the olefin. The molecular weight can also be lowered by raising the temperature, again in a known manner.

The polymerisation is carried out in solution, with the butene-1 or  $C_4$ -fraction acting as solvent for the polymer and solvent/suspending agent for the catalyst, continuously or discontinuously.

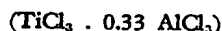
The largely amorphous homopolymers, co-

polymers and terpolymers of butene-1 obtained by the process according to the invention contain as a rule 60 to 98%, preferably 70 to 95%, of ether-soluble constituents.

- 5 The process readily permits the production of a largely amorphous butene-1 polymer with RSV values of 0.3 to 0.6 dl/g, which is an optimum product for numerous applications; it also permits, without difficulty, the production of polymers of RSV values outside this narrow range. This can be seen from the following Examples which illustrate the invention and in which percentages are by weight.

15 Example 1

- Butene-1 is polymerised in 120 parts by weight of butene-1 (98% strength) at 100°C and a total pressure of 19 to 15 atmospheres gauge, in a stirred kettle, by means of a mixed contact catalyst of 0.003 part by weight of a crystalline titanium trichloride in the form of a commercially available aluminium-reduced  $TiCl_3$ ,



- 25 and 0.01 part by weight of aluminium triisobutyl. After a polymerisation time of 3 hours the polymerisation is stopped by adding 0.1 part by weight of water. The unconverted butene is evaporated in an evaporator and the melt of the largely amorphous poly-

- 60 RSV  
Ether extract  
Penetration  
Melt viscosity  
Proportion of butene-2

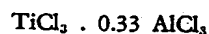
butene-1 is run out at a temperature of 150°C. The polybutene-1, obtained at a conversion of 91%, has the following properties:

RSV	0.6 dl/g	$\bar{M}_v$ : 150,000
Ether extract	78%	
Penetration	13.2	
Melt viscosity	85,000 cP/170°C	

35

Example 2

Butene-1 is polymerised in 120 parts by weight of a  $C_4$ -cut which contains 47% of butene-1, 45% of butene-2 and 8% of butane, with the aid of a mixed contact catalyst of 0.02 part by weight of a crystalline titanium trichloride



45

and 0.072 part by weight of aluminium triisobutyl, in a pressure-resistant stirred kettle at a temperature of 80 to 120°C, a partial pressure of hydrogen of 0.2 atmosphere and a total pressure of 12 atmospheres gauge. After a polymerisation time of 2 hours, the unconverted butene-butane mixture is evaporated off at temperatures up to 120°C. The melt of the largely amorphous polybutene-1 is run out as a liquid at this temperature. The conversion is 90%. The polybutene-1 has the following properties:

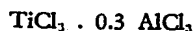
50

55

1.1 dl/g	$\bar{M}_v$ : 350,000
68%	
12.6	
184,000 cP/170°C	
0	

Example 3

- 65 2.6 parts by weight of a  $C_4$ -cut which contains 49% of butene-1, 43% of butene-2 and 8% of butane, 0.25 part by weight of propene, 0.00004 part by weight of a crystalline



- 70 and 0.00014 part by weight of aluminium triisobutyl are introduced hourly into a pressure-resistant stirred kettle at 60°C. The polymerisation is carried out at a partial pressure of hydrogen of 2 atmospheres and a total pressure of 9 atmospheres gauge. After

an average dwell time of 18 hours, the polymer solution is run continuously via a shut-off device, controlled by the level in the polymerisation kettle, into a falling stream evaporator in which 0.004 part by weight of a 10 per cent strength aqueous ammonia solution are additionally vaporised hourly. The unconverted hydrocarbons and low-boiling oligomers are separated off at a temperature of 190°C and the melt of the largely amorphous butene-1/propene copolymer is run out. 1 part by weight of a largely amorphous polymer having the following properties is obtained hourly:

80

85

- 90 RSV  
Ether extractables  
Penetration  
Melt viscosity  
Proportion of propene  
Softening point  
(ring and ball)
- 0.35 dl/g  $\bar{M}_v$ : 90,000  
93%  
18  
9,000 cP/170°C  
approx. 16%  
86°C

95

If the polymerisation is carried out without added hydrogen, a largely amorphous butene-1/propene copolymer with an RSV value of 3.1 dl/g is obtained.

5

#### Example 4

Butene-1 is polymerised in 120 parts by weight of butene-1 (98% strength) with the aid of a mixed contact catalyst of 0.005 part by weight of a crystalline

10

$\text{TiCl}_3 \cdot 0.33 \text{ AlCl}_3$

and 0.016 part by weight of aluminium tri-

25

RSV  
Ether extractables  
Penetration  
Melt viscosity  
Brittle point according to  
Fraass  
Ethene content about

30

n-butyl in a pressure-resistant stirred kettle at 90°C and a pressure of 17 to 12 atmospheres gauge. During the polymerisation time of 3 hours, 2.5 parts by weight of ethylene are added. The polymerisation is then stopped by adding 0.1 part by weight of 10 per cent strength aqueous ammonia solution. The unconverted ethylene and butene-1 and small proportions of low-boiling oligomers are separated off at 140°C in an evaporator. The largely amorphous polymer obtained with 59% conversion has the following properties:

15

20

0.5 dl/g  $\bar{M}_v$ : 132,000  
92%  
34  
32,000 cP/170°C  
-45°C  
2%

If instead of the aluminium tri - n - butyl an equimolecular amount of aluminium tri-propyl is employed, comparable products are obtained.

35

$\text{TiCl}_3 \cdot 0.5 \text{ AlCl}_3$

and 0.025 part by weight of aluminium tri-ethyl the polymerisation is carried out at 90°C under a pressure of 16 to 12 atmospheres gauge, 1 part by weight of ethylene being added. After a polymerisation time of 3 hours the unconverted hydrocarbons are removed together with the low-boiling oligomers at a temperature of 110°C. A largely amorphous butene - propene - ethene terpolymer having the following properties is obtained, the conversion being 86%.

45

50

55

#### Example 5

A mixture of 150 parts by weight of a  $C_4$ -cut consisting of 54% of butene-1, 39% of butene-2 and 7% of butane, and 4 parts by weight of propene is initially introduced into a pressure-resistant stirred kettle. After addition of 0.015 part by weight of a crystalline titanium trichloride

40

RSV  
Ether extractables  
Penetration  
Melt viscosity  
Brittle point according to  
Fraass  
Propene content about  
Ethene content about

60

0.6 dl/g  $\bar{M}_v$ : 150,000  
81%  
27  
51,000 cP/170°C  
-47°C  
4%  
1%

#### Example 6

Butene is copolymerised with hexene-1 in a solution of 110 parts by weight of butene-1 (98% strength) and 5 parts by weight of hexene-1 at a temperature of 70 to 90°C and a pressure of 9 atmospheres gauge, using a mixed contact catalyst of 0.01 part by weight of a crystalline titanium trichloride

65

70

$\text{TiCl}_3 \cdot 0.56 \text{ AlCl}_3$

prepared by reduction of titanium tetrachloride with ethyl-aluminium sesquichloride at -5°C and subsequent heat treatment at 130°C, and 0.035 part by weight of aluminium triisobutyl. After a polymerisation time of 2 hours, the polymerisation is stopped by adding 0.1 part by weight of water and the unconverted monomers are blown off. A largely amorphous butene-1/hexene-1 copolymer having the following properties is obtained, the conversion being 74%:

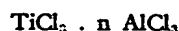
75

80

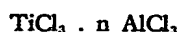
	RSV	1.6 dl/g	$\bar{M}_v$ : 574,000
	Ether extractables	88%	
	Penetration	26	
	Melt viscosity	67,000 cP/20°C	
5	Brittle point	-42°C	
	Hexene content about	6%	

# WHAT WE CLAIM IS:—

1. A process for the manufacture of a largely amorphous butene-1 polymer by the low pressure method, wherein butene-1 is homopolymerised or is copolymerised with from 0.1 to 30 per cent by weight based on butene-1 of one or more other  $\alpha$ -mono-olefins as comonomers at a temperature of from 40 to 120°C in bulk or in solution in a  $C_4$ -fraction comprising butene-2 and/or butane in addition to butene-1 using a mixed catalyst consisting of

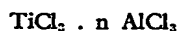


- 20 (n=0.2 to 0.6) and an aluminium trialkyl with  $C_2$  to  $C_4$  alkyl groups, at an atomic ratio of Al in the aluminium trialkyl:Ti in the

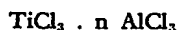


- 25 of 1.2:1 to 5:1 and a concentration of 0.01 to 1 mmol of  $TiCl_3$  per litre of total liquid phase.

2. A process as claimed in claim 1 wherein the



- 30 employed is a crystalline titanium trichloride.
3. A process as claimed in claim 2 wherein the



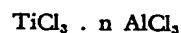
employed is a crystalline

- 35  $TiCl_3 \cdot 0.33 AlCl_3$

obtained by reduction of  $TiCl_3$  with aluminium.

4. A process as claimed in any of claims 1 to 3 wherein aluminium triisobutyl is employed as the aluminium trialkyl.

5. A process as claimed in any of claims 1 to 4 wherein an atomic ratio of Al in the aluminium trialkyl:Ti in the

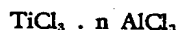


of 1.5:1 to 3.0:1 is employed.

6. A process as claimed in any of claims 1 to 5 wherein propene and/or ethene are employed as comonomer(s).

7. A process as claimed in any of claims 1 to 6 wherein the butene-1 with or without comonomer(s) is employed in solution in a  $C_4$  fraction containing at least 40% by weight of butene-1.

8. A process as claimed in any of claims 1 to 7 wherein the



is employed at a concentration of 0.05 to 0.3 m mol of  $TiCl_3$  per litre of total liquid phase.

9. A process as claimed in any of claims 1 to 8 wherein the molecular weight is regulated during the polymerisation by addition of hydrogen to the olefin.

10. A process for the manufacture of a largely amorphous butene-1 polymer substantially as described in any of the foregoing Examples.

11. Largely amorphous butene-1 polymers when manufactured by a process as claimed in any of claims 1 to 10.

J. Y. & G. W. JOHNSON,  
Furnival House,  
14—18, High Holborn,  
London, WC1V 6DE,  
Chartered Patent Agents,  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.